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Softener Absorption by Regenerated Cellulose. Uptake from 10% Aqueous Glycerol*

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INTRODUCTION

Cellulose regenerated from viscose solution by acids dries to a hard brittle material. Commercial cellophane sheet is therefore plasticized by water and certain other simple molecules, commonly called softeners in the trade. Glycerol as a softener is defined also as a humectant, and the word *cellophane* is legally restricted to a regenerated cellulose film containing such a humectant. For many years, the precise mechanism by which water and softeners are absorbed and held in regenerated cellulose has been a puzzle, and a great amount of study has failed to elucidate this problem entirely.

In 1933, Shutt and Mack[1] concluded from a study of dried cellophanes subsequently softened with glycerol or one of several glycols that the softeners were not held by chemical combination with cellulose but rather by adsorption. Unfortunately for this theory, however, the adsorption isotherms plotted showed no flattening in concentrated softener bath solutions; the softener content continued to rise with the highest concentrations studied, approximately 4.25 molar. A sharp initial rise, to be expected in such cases with dry film, was observed, but it accounted for only a very small amount of the softener ultimately imbibed, equivalent to about three per cent of the cellulose involved.

This question has been reopened on several occasions since then. Studies of the sorption of small molecules by cellulose, and on hydrogen bonding in cellulose, have shown that in the presence of large amounts of water, water molecules are bound so firmly to cellulose that adsorption of other solutes does not normally occur.[2-5]

A statistical treatment of polymer-liquid mixtures applied to the cellulose-water system has been given.[6] At very high vapor pressures of water, the system can best be analyzed in terms of a polymer-liquid mixture. This is the situation which would seem to correspond to the gel film with which the present work is concerned.

A study of the permeability of cellophane to liquids from aqueous solutions has shown that the permeability depends upon the void volume and thickness of the swollen cellophane membrane.[7] The role of adsorption was not considered.

The question of softener uptake by gel film was also investigated by Danilov, Sokolovskiĭ, and Evdokimova,[8] who found an increase in volume and enrichment of glycerol concentration within the cellulosic body with increasing concentration in the softener bath. Otherwise stated, these investigators found a special affinity of wet cellulose for molecules of glycerol, i.e., an ability of gel film to concentrate glycerol; at the lowest concentration studied, 8%, the enrichment factor was 1.29. This work must be read carefully, being somewhat confusing in terminology, since the authors studied a so-called swelling of gel film by glycerol solutions and defined "swelling" as a fractional increase in weight.

The relationship of water and cellulose in swollen gel film has never been satisfactorily explained. The simplest process of softener uptake by gel film would involve the replacement of water by softener solution from the impregnating bath by establishment of a dynamic diffusion equilibrium. Indeed the simple premise of *no* enrichment seemed to us the most reasonable one to adopt, in the absence of any compelling contrary evidence. On this assumption the amount of softener taken up is the product of two variables, the concentration of the softener bath and the volume of free space in the cellulosic structure to be filled, assuming of course that the water in the gel film equilibrating with the bath is a negligible quantity by comparison with the amount of water in the softener bath.

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Therefore, to arrive at an explanation of softener absorption verifiable experimentally, it was necessary to find a method of measuring accurately the amount of free space in gel film, and to ascertain whether the amount of softener absorbed is determined by the volume. Such a determination permits conclusions to be made regarding some factors in softener absorption by regenerated cellulose and about the existence of an enrichment factor.

GEL FILM VOLUME AND SOFTENER UPTAKE

It is known that gel film shrinks during the removal of water on drying and that this shrinkage occurs to a much larger degree in thickness than in length or width. Thus the film volume depends largely on the state of collapse of the structure, which will be determined by the amount of softener present in the film and the moisture content after drying. Conversely, the amount of softener picked up during impregnation depends upon the available volume, which in turn is determined by the type of gel film used and the state of collapse of the cellulose structure at the time of impregnation with softener.

Gel film usually contains a mass of water at least three times the weight of cellulose. It is inferred, therefore, that the free volume in gel film is about 3 ml. per gram of cellulose. It was found in the present study that the ratio of softener concentration in the bath to softener content in the film becomes nearly constant (equal to about 3), if the softener content in the film is expressed as grams per 100 grams of cellulose and the bath content is expressed as grams per 100 ml. of solution.

We have found that several different organic compounds containing hydroxyl or amino groups have pickup ratios (defined below) of 3.2 ± 0.2, indicating a nearly constant volume relationship.[9] This pickup ratio of approximately 3 obtained for several types of softeners indicates that the free volume associated with cellulose bears a significant relationship to softener uptake. Another correlation of softener content and volume is indicated by the fact that equal areas of dried film containing approximately equal weights of cellulose vary in thickness in direct proportion to the softener content.

To establish the mode of softener pickup, an intensive series of impregnation experiments was done, a 10.0% aqueous solution of glycerol being used. The precise initial and final water content, the final softener content, and the dry cellulose weight were determined by weighings and analyses described below.

EXPERIMENTAL

Materials and Methods

Gel Film

The cellophane used was undried, unsoftened gel film from our Pisgah Forest plant. The degree of polymerization of this film was between 400 and 500. The degree of polymerization was determined by a modification of the method of Battista[10] involving the use of cupriethylenediamine. A rapid dispersion of cellulose in cupriethylenediamine is achieved by use of small amounts of Aerosol OT added to the distilled water used.[11] The sample is dried in vacuum at 50–60°C. for at least 3 hours; the moisture in the sample is assumed to be 0.8%. The concentration of cellulose in 0.5 *N* cupriethylenediamine is kept as close as possible to 0.500 g./100 ml. (The specific gravity of this solution is 1.052.) From the absolute viscosity measured in centipoises with an Ostwald viscosimeter (200–1000 seconds) the degree of polymerization is calculated. A typical analysis gave a value of 430 units.

Glycerol

Reagent grade glycerol from Allied Chemical Corporation was used. The moisture content was found to be 5.44% and was corrected for in all preparations of solutions. Glycerol analyses were carried out by periodic acid oxidation[12] of the film extracts or by differential weighing as described below. All analyses are reported in per cent by weight.

Procedure

A sample of gel film 4.0 inches square was cut with the aid of a template, surface water was blotted off, and the weight was determined; the sample was reimmersed in water, blotted and weighed. The film was then immersed in the 10.0% glycerol bath for at least 10 minutes, blotted, and again weighed on an analytical balance. The glycerol picked up was determined by eluting the softener from the sample by immersing and washing it with water and analyzing the total washings. The film was then dried to constant weight in a vacuum oven (45 minutes) at 95°C. to obtain the

TABLE I
Softener Pickup of Gel Film from a 10.0% Glycerol Bath at 20°C.

	Film Sample, Five Determinations Each				
	1	2	3	4	5
Weight of gel film, mg.	808	843	846	1100	1098
Weight of cellulose, mg.	208	206	209	239	238
Weight of water, mg.	600	637	637	861	860
Free volume, mm.^{3}	600	637	637	861	860
Weight of impregnated film, mg.	817	864	866	1120	1117
Weight of glycerol, mg.	62	71	68	90	91
Weight of water in solution, mg.	547	587	589	791	788
Weight of water and glycerol, mg.	609	658	657	881	879
Glycerol in film solution, %	10.2	10.8	10.3	10.2	10.3
Density of solution	1.023	1.023	1.023	1.023	1.023
Free volume after impregnation, mm.^{3}	595	642	642	862	859
Enrichment factor[a]	1.02	1.08	1.03	1.02	1.03
Swelling factor[b]	0.99	1.01	1.01	1.00	1.00

[a] Enrichment factor $= \frac{\text{per cent glycerol in film}}{\text{per cent glycerol in bath}}$.

[b] Swelling factor $= \frac{\text{free volume after impregnation}}{\text{free volume before impregnation}}$.

weight of dry cellulose; the initial and final water contents were found by difference.

Another method used to determine the softener content consisted in drying the softened film to constant weight in the vacuum oven. (After 120 minutes at 60°C., all of the water had been expelled.) After the softener had been washed out and the film had been dried to constant weight, the softener content was obtained by difference. This method of softener determination was found to be in good agreement with the direct analytical method but was applicable only to the less volatile softeners, such as glycerol. From this experimental procedure the following data were obtained or could be calculated: (1) water content of unsoftened and softened film, (2) softener content of impregnated gel film, (3) cellulose content of softened film.

From these data and the known densities of water and softener solution, the available volume of gel film was determined and compared with the calculated volume of the softened film. This method of determining free volume is independent of gauge and area measurements and is a fairly precise method; it depends, however, upon careful weighings and its accuracy is impaired slightly by the small loss of water during the time required to weigh wet gel film. Weighings were made as quickly as possible, and in this work no corrections for losses were made. The experimental data for five different gel film samples are summarized in Table I. The data for each film sample are an average of the values from determinations made on five specimens.

Changes in density resulting from monolayer adsorption of either water or glycerol inside the film are not considered here. A subsequent, more exact, treatment of volume changes[9] shows that these effects are small and constant for both water- and glycerol-softened films. Thus any correction factor applied to the free volume before and after softening drops out, since the swelling factor is a ratio of these two volumes.

Rate of Softener Absorption

In order to show that rate of diffusion was not an important factor in this study, it was necessary to study the rate of establishment of equilibrium.

Gel film samples of known weight were dipped into 10.0% glycerol solution for a measured period of time, rinsed in water, blotted as quickly as possible, and reweighed to give the residual glycerol content. The time for rinsing and blotting was standardized to within one second. Much of the glycerol on the film surface was removed in this procedure, and only the amount which had penetrated the film remained. In this way, increasing amounts of glycerol were found on soaking up to 25 seconds, in 4-second increments, but no significant increase was found beyond 25 seconds. The time to establish equilibrium was therefore considered to be about 25 seconds. A direct chemical analysis for glycerol was done for some samples; the agreement with the weighing method was excellent.

SWELLING FACTOR

The data of Table I show that softener pickup by gel film occurs by replacement of water by an aqueous solution of softener without change in volume. The swelling factor, defined as the ratio of free volume of gel film after impregnation to free volume before impregnation was measured for 10 samples of gel film and found to be $0.99_3 \pm 0.01$.

These measurements indicate a very slight shrinkage of free volume of less than one per cent, which is probably insignificant. It appears therefore that no change of free volume occurs during the impregnation of gel film by glycerol from a 10.0% softener bath.

ENRICHMENT FACTOR

The data presented in Table I indicate that the solution within the film undergoes slight enrichment, approximately 0.03% over the concentration of glycerol in the bath, i.e., an enrichment factor of 1.03–1.04, or less than one-seventh that previously reported.[8] (The enrichment factor is defined as the ratio of percentage of softener in solution in the gel film to the percentage of softener in the softener bath.)

This initial observation was of interest to us since such a measurement might provide an insight into the mechanism of softener uptake. A more thorough study of absorption from a 10% glycerol solution showed that the enrichment was generally less than 0.05%, and sometimes zero. The average enrichment factor for 14 different gel film samples was 1.03_6 (Table II).

The enrichment factor was similarly determined at the 10% level for three other organic compounds (Table III). Although the values are not far from unity, on the average there seems to be a slight enrichment.

TABLE II
Enrichment Factors for 10% Glycerol

Sample	Enrichment Factor
1	1.02
2	1.08
3	1.03
4	1.02
5	1.03
6	1.05
7	1.05
8	1.06
9	1.00
10	1.05
11	1.09
12	1.05
13	1.00
14	1.00
Average	1.03_6

TABLE III
Enrichment Factor for Various Organic Compounds

Compound	Enrichment Factor
Glycerol	1.04
Propylene glycol	1.00
Triethylene glycol	0.96
Triethanolamine	1.16

The great enrichment of glycerol in gel film observed by others[8] may perhaps be explained by the fact that their film samples were prepared in relatively small quantity by a laboratory method, wheras our gel film samples were from a full-scale cellophane casting machine. The film had therefore a different fine structure and perhaps a higher absorption ability. The discrepancy can also be explained by an excessive loss of water during the weighing process; this loss diminishes with increasing softener content.

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Synopsis

The softener content of regenerated cellulose film (gel film) in equilibrium with aqueous glycerol solution was found to be determined primarily by only two factors: the softener concentration of the solution and the volume of free space within the gel film. Volume changes of film in contact with 10% glycerol solutions are negligible. Preferen-

tial uptake of glycerol as the solution passes into the film is, at most, slight, amounting to no more than 0.04% at the concentration used. No evidence was found for a large enrichment within the gel film, as has been postulated, or for adsorption of glycerol on cellulose chains. The system, cellulose-glycerol-water, appears to be a polymer-liquid mixture brought to equilibrium principally by diffusion. It appears that at 10% concentration, glycerol and probably other organic compounds are taken in by gel film by a diffusion process in which the free water in the film is replaced by solution without appreciable enrichment or change in volume. Water contained in the interchain spaces of cellulose is simply exchanged for softener solution. The free volume of the film as determined by the cellulose structure and the degree of crystallinity remains essentially unchanged on softener uptake at the softener concentration studied.

Résumé

La teneur en émollient d'un film de cellulose régénérée en équilibre avec une solution aqueuse de glycérine est déterminée primairement par deux facteurs: la concentration en émollient dans la solution et le volume d'espace libre à l'intérieur du film gelifié. La variation de volume d'un film en contact avec une solution de 10% de glycérine est négligeable. L'absorption préférentielle de la glycérine lorsque la solution passe à travers le film n'atteint, quoique, lentement que 0.04% aux concentrations utilisées. Aucune preuve n'est trouvée pour un grand enrichissement dans le film gelifié comme il avait été supposé ni pour une adsorption de glycérine sur les chaînes cellulosiques. Le système, cellulose-glycerine-eau se trouve être un mélange liquide-polymère porté à équilibre principalement par diffusion. Il semble qu'à une concentration de 10%, la glycérine et (provablement les autres composés organiques) sont pris dans le film gelifié par un processus de diffusion dans lequel l'eau du film est remplacée par la solution et cela sans enrichissement appréciable et sans variation de volume. L'eau contenue dans les espaces intercaténaires de la cellulose est simplement échangée avec la solution émolliente. Le volume libre du film est déterminé par la structure de la cellulose et le degré de cristallinité reste inchangé après l'absorption d'émollient aux concentrations envisagées.

Zusammenfassung

Der Weichmachergehalt eines regenerierten Cellulosefilms (Gelfilm) im Gleichgewicht mit einer wässrigen Glycerinlösung ist, wie gefunden wurde, in erster Linie lediglich durch zwei Faktoren bestimmt: durch die Weichmacherkonzentration der Lösung und durch die Grösse des freien Volumens innerhalb des Gelfilms. Volumsänderungen des Films bei Berührung mit 10%igen Glycerinlösungen können vernachlässigt werden. Bevorzugte Aufnahme von Glycerin beim Übergang der Lösung in den Film ist auch im äussersten Fall nur schwach und beträgt bei den verwendeten Konzentrationen nicht mehr als 0.04%. Es wurde kein Hinweis auf eine starke Anreicherung innerhalb der Gelfilme, wie sie schon angenommen worden war, oder auf eine Adsorption von Glycerin an Celluloseketten gefunden. Das System Cellulose-Glycerin-Wasser ist offenbar eine Polymer-Flüssigkeitsmichung, deren Gleichgewicht in der Hauptsacht durch Diffusion eingestellt wird. Es scheint, dass bei einer Konzentration von 10% Glycerin (und wahrscheinlich auch andere organische Verbindungen) von dem Gelfilm durch einen Diffusionsprozess aufgenommen werden, bei welchem das freie Wasser im Film durch die Lösung ohne nennenswerte Anreicherung oder Volumsänderung ersetzt wird. Wasser, das in den Zwischenkettenbereichen der Cellulose enthalten ist, wird einfach gegen die Weichmacherlösung ausgetauscht. Das freie Volumen des Films wird durch die Struktur der Cellulose und den Kristallinitätsgrad bestimmt und erfährt bei den untersuchten Weichmacherkonzentrationen durch die Aufnahme des Weichmachers keine wesentliche Änderung.

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